

What is claimed is:

1. A copper-plating liquid free from an alkali metal and a cyanide, comprising divalent copper ions and a complexing agent.

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2. The copper-plating liquid according to claim 1, further comprising a pH adjusting agent free from an alkali metal and a cyanide, selected from the group consisting of sulfuric acid, hydrochloric acid, phosphoric acid, cholin, ammonia and tetramethyl ammonium hydroxide.

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3. The copper-plating liquid according to claim 1, wherein a concentration of said divalent copper ions is in the range of 0.1-100 g/l, a concentration of said complexing agent is in the range of 0.1-500 g/l, and a pH of the copper-plating liquid is in the range of 7-14.

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4. The copper-plating liquid according to claim 1, further comprising at least one additive selected from the group consisting of organic acids, amines, glycerin, gelatin, heavy metal ions, thiazoles, triazoles, thiadiazoles, imidazoles, pyrimidines, sulfonic acids, and gultamic acids.

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5. The copper-plating liquid according to claim 1, wherein said complexing agent is selected from the group consisting of ethylenediamine tetracetic acid, ethylenediamine, N,N',N'',N'''-ethylene-di-nitro-tetrapropene-2-ol, pyrophosphoric acid, iminodiacetic acid, diethylenetriamine

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pentacetic acid, diethylenetriamine, triethylenetetramine,
tetraethylenepentamine, diamino butane, hydroxyethyl
ethylenediamine, ethylenediamine tetrapropionic acid,
ethylenediamine tetramethylene phosphonic acid,
5 diethylenetriamine tetramethylene phosphonic acid,
diethylenetriamine pentamethylene phosphonic acid, and their
derivatives.

6. The copper-plating liquid according to claim 5, further
10 comprising a pH adjusting agent free from an alkali metal and a
cyanide, selected from the group consisting of sulfuric acid,
hydrochloric acid, phosphoric acid, cholin, ammonia and
tetramethyl ammonium hydroxide.

15 7. The copper-plating liquid according to claim 5, wherein
a concentration of said divalent copper ions is in the range of
0.1-100 g/l, a concentration of said complexing agent is in the
range of 0.1-500 g/l, and a pH of the copper-plating liquid is in
the range of 7-14.

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8. The copper-plating liquid according to claim 5, further
comprising at least one additive selected from the group consisting
of organic acids, amines, glycerin, gelatin, heavy metal ions,
thiazoles, triazoles, thiadiazoles, imidazoles, pyrimidines,
25 sulfonic acids, and glutamic acids.

9. A method for plating a substrate having fine recesses,
in a surface of the substrate thereof, covered with a barrier layer

and/or a seed layer to fill said fine recesses with a metal, comprising:

plating the surface of the substrate in a first-stage by contacting the substrate in a first plating liquid; and

5 plating the surface of the substrate in a second-stage by contacting the substrate in a second plating liquid, wherein said first plating liquid has a higher polarization than said second plating liquid.

10 10. The method according to claim 9, wherein said first plating liquid is free from an alkali metal and a cyanide, and comprises divalent copper ions and a complexing agent.

15 11. The method according to claim 9, wherein said first plating liquid further comprises a pH adjusting agent free from an alkali metal and a cyanide, selected from the group consisting of sulfuric acid, hydrochloric acid, phosphoric acid, cholin, ammonia and tetramethyl ammonium hydroxide.

20 12. The method according to claim 9, wherein said first plating liquid has a divalent copper ion concentration of 0.1-100 g/l and a complexing agent concentration of 0.1-500 g/l, and has a pH of 7-14.

25 13. The method according to claim 9, wherein said first plating liquid further comprises at least one additive selected from the group consisting of organic acids, amines, glycerin, gelatin, heavy metal ions, thiazoles, triazoles, thiadiazoles,

imidazoles, pyrimidines, sulfonic acids, and glutamic acids.

14. The method according to claim 9, wherein said complexing agent contained in said first plating liquid is selected from the group consisting of ethylenediamine tetracetic acid, ethylenediamine, N,N',N'',N'''-ethylene-di-nitro-tetrapropane-2-ol, pyrophosphoric acid, iminodiacetic acid, diethylenetriamine pentacetic acid, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, diamino butane, hydroxyethyl ethylenediamine, ethylenediamine tetrapropionic acid, ethylenediamine tetramethylene phosphonic acid, diethylenetriamine tetramethylene phosphonic acid, diethylenetriamine pentamethylene phosphonic acid, and their derivatives

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15. The method according to claim 14, wherein said first plating liquid further comprises a pH adjusting agent free from an alkali metal and a cyanide, selected from the group consisting of sulfuric acid, hydrochloric acid, phosphoric acid, cholin, ammonia and tetramethyl ammonium hydroxide.

16. The method according to claim 14, wherein said first plating liquid has a divalent copper ion concentration of 0.1-100 g/l and a complexing agent concentration of 0.1-500 g/l, and has a pH of 7-14.

17. The method according to claim 14, wherein said first plating liquid further comprises at least one additive selected

from the group consisting of organic acids, amines, glycerin, gelatin, heavy metal ions, thiazoles, triazoles, thiadiazoles, imidazoles, pyrimidines, sulfonic acids, and glutamic acids.

5 18. A method for plating a substrate having fine recesses, in a surface of the substrate thereof, covered with a barrier layer and/or a seed layer to fill said fine recesses with a metal, comprising:

 plating the surface of the substrate by contacting the
10 substrate in a plating liquid having an excellent uniform electrodeposition property.

 19. The method according to claim 18, wherein said plating liquid is free from an alkali metal and a cyanide, and comprises
15 divalent copper ions and a complexing agent.

 20. The method according to claim 18, wherein said plating liquid further comprises a pH adjusting agent free from an alkali metal and a cyanide, selected from the group consisting of sulfuric
20 acid, hydrochloric acid, phosphoric acid, cholin, ammonia and tetramethyl ammonium hydroxide.

 21. The method according to claim 18, wherein said plating liquid has a divalent copper ion concentration of 0.1-100 g/l and
25 a complexing agent concentration of 0.1-500 g/l, and has a pH of 7-14.

 22. The method according to claim 18, wherein said plating

liquid further comprises at least one additive selected from the group consisting of organic acids, amines, glycerin, gelatin, heavy metal ions, thiazoles, triazoles, thiadiazoles, imidazoles, pyrimidines, sulfonic acids, and glutamic acids.

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23. The method according to claim 18, wherein said complexing agent contained in said plating liquid is selected from the group consisting of ethylenediamine tetracetic acid, ethylenediamine, N,N',N'',N'''-ethylene-di-nitro-tetrapropane-2-ol,
10 pyrophosphoric acid, iminodiacetic acid, diethylenetriamine pentacetic acid, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, diamino butane, hydroxyethyl ethylenediamine, ethylenediamine tetrapropionic acid, ethylenediamine tetramethylene phosphonic acid,
15 diethylenetriamine tetramethylene phosphonic acid, diethylenetriamine pentamethylene phosphonic acid, and their derivatives.

24. The method according to claim 23, wherein said plating
20 liquid further comprises a pH adjusting agent free from an alkali metal and a cyanide, selected from the group consisting of sulfuric acid, hydrochloric acid, phosphoric acid, choline, ammonia and tetramethyl ammonium hydroxide.

25 25. The method according to claim 23, wherein said plating liquid has a divalent copper ion concentration of 0.1-100 g/l and a complexing agent concentration of 0.1-500 g/l, and has a pH of 7-14.

26. The method according to claim 23, wherein said plating liquid further comprises at least one additive selected from the group consisting of organic acids, amines, glycerin, gelatin,
5 heavy metal ions, thiazoles, triazoles, thiadiazoles, imidazoles, pyrimidines, sulfonic acids, and glutamic acids.

27. A plating apparatus comprising:

a first plating section for plating a surface of a substrate
10 having fine recesses formed in the surface thereof and covered with a barrier layer and/or a seed layer in a first-stage;

a first plating liquid feed section for feeding a first liquid into a plating chamber in said first plating section;

a second plating section for plating the surface of the
15 substrate which has undergone said first-stage plating in a second-stage;

a second plating liquid feed section for feeding a second plating liquid into a plating chamber in said second plating section; and

20 a transport section for transporting the substrate from said first plating section to said second plating section, wherein said first plating liquid has a higher polarization than said second plating liquid.

25 28. The plating apparatus according to claim 27, wherein said first plating liquid is free from an alkali metal and a cyanide, and comprises divalent copper ions and a complexing agent.

29. The plating apparatus according to claim 27, wherein said first plating liquid further comprises a pH adjusting agent free from an alkali metal and a cyanide, selected from the group consisting of sulfuric acid, hydrochloric acid, phosphoric acid, cholin, ammonia and tetramethyl ammonium hydroxide.

30. The plating apparatus according to claim 27, wherein said first plating liquid has a divalent copper ion concentration of 0.1-100 g/l and a complexing agent concentration of 0.1-500 g/l, and has a pH of 7-14.

31. The plating apparatus according to claim 27, wherein said first plating liquid further comprises at least one additive selected from the group consisting of organic acids, amines, glycerin, gelatin, heavy metal ions, thiazoles, triazoles, thiadiazoles, imidazoles, pyrimidines, sulfonic acids, and gultamic acids.

32. The plating apparatus according to claim 27, wherein said complexing agent contained in said first plating liquid is selected from the group consisting of ethylenediamine tetracetic acid, ethylenediamine, N,N',N'',N'''-ethylene-di-nitro-tetrapropane-2-ol, pyrophosphoric acid, iminodiacetic acid, diethylenetriamine pentacetic acid, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, diamino butane, hydroxyethyl ethylenediamine, ethylenediamine tetrapropionic acid, ethylenediamine tetramethylene phosphonic acid, diethylenetriamine tetramethylene phosphonic acid,

diethylenetriamine pentamethylene phosphonic acid, and their derivatives.

33. The plating apparatus according to claim 32, wherein said
5 first plating liquid further comprises a pH adjusting agent free from an alkali metal and a cyanide, selected from the group consisting of sulfuric acid, hydrochloric acid, phosphoric acid, cholin, ammonia and tetramethyl ammonium hydroxide.

10 34. The plating apparatus according to claim 32, wherein said first plating liquid has a divalent copper ion concentration of 0.1-100 g/l and a complexing agent concentration of 0.1-500 g/l, and has a pH of 7-14.

15 35. The plating apparatus according to claim 32, wherein said first plating liquid further comprises at least one additive selected from the group consisting of organic acids, amines, glycerin, gelatin, heavy metal ions, thiazoles, triazoles, thiadiazoles, imidazoles, pyrimidines, sulfonic acids, and
20 gultamic acids.

36. A plating apparatus comprising:

a loading/unloading section for loading and unloading a semiconductor substrate;

25 a first metal plating unit for forming a first plated metal film on a surface of the semiconductor substrate;

a second metal plating unit for forming a second plated metal film on said first plated metal film;

a bevel-etching unit for etching away a metal film formed on the edge portion of the semiconductor substrate which has said second plated metal film on the surface thereof;

an annealing unit for annealing said semiconductor substrate; and

a transporting device for transporting said semiconductor substrate, wherein said first metal plating liquid for forming said first plated metal film has a higher polarization than said second metal plating liquid for forming said second plated metal film.

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37. A plating method, comprising:

forming a first plated metal film on a surface of a semiconductor substrate;

forming a second plated metal film on said first plated metal film;

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etching away a metal film formed on the edge portion of the semiconductor substrate which has said second plated metal film on the surface thereof; and

annealing the bevel-etched semiconductor substrate, wherein said first metal plating liquid for forming said first plated metal film has a higher polarization than said second metal plating liquid for forming said second plated metal film.

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